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Abstract

The effect of the application of a DC current on the annealing of point defects in Ni_3Ti was investigated by positron annihilation spectroscopy (PAS). An increased rate of point defect annealing is observed under the influence of a current and is attributed to a 24% decrease in the mobility activation energy. The results are interpreted in terms of the electron wind effect and the complex nature of diffusion in ordered intermetallic phases. This work represents the first direct evidence of the role of the current on the mobility of point defects in intermetallic systems.

1. Introduction

Recent studies have shown a considerable effect of high electric current fluxes on solid-state reactivity in metallic systems [1-5]. Interest in such an effect was motivated by concerns on failure of interconnects due to electromigration in electronic applications and by the potential of using a current in novel processing techniques. Moreover, several

fundamental aspects of the role played by the current in reactivity enhancement are not well understood. In this paper we present the first evidence of the effect of the current on point defect mobility in an intermetallic system.

Experiments have been conducted in which metal-metal diffusion couples are reacted isothermally but with varying DC current densities [1-3]. These reactive diffusion experiments permit the study of current density effects on phase formation kinetics that are not related to Joule heating effects. In the Au-Al system [2, 3], the reaction between the elements required an incubation time for product nucleation, a time which was significantly reduced, and in some cases eliminated, by the application of a current. No change in activation energy for phase growth was observed in this system. In contrast, in the Ni-Ti system [1] the increase in growth rates of product phase formation was associated with a decrease in the effective activation energy when a current was imposed. Both observations indicate current-enhanced reactivity. In these studies, however, it was not possible to gain insight on the role played by the current since the general expectations of electromigration were not realized directly. The enhanced kinetics observed in these studies were independent of the direction of the DC current so the role of electromigration is not easily identified. Despite these experiments and others showing the enhancement of the reaction kinetics in metallic systems with current, the intrinsic role of the role current cannot be ascertained because of the difficulty in decoupling the large effect of Joule heating from the intrinsic effects of the current.

It was suggested that the current increases the concentration and/or mobility of point defects thus aiding mass transfer and enhancing intermetallic growth [1, 3]. There is experimental evidence that high-density current flux increases point defect concentration in metallic conductors. Asoka-Kumar et al. [6] found a significant increase in point defect concentration in the Al-Cu system when it was subjected to a current. In this article we focus on the latter proposal—that an applied current enhances vacancy mobility in the Ni-Ti system. Our approach was to conduct defect relaxation experiments in which highly defected samples are annealed at different temperatures with and without an applied current and analyzing the samples using Positron Annihilation Spectroscopy (PAS). Isothermal annealing of thermal vacancies has been utilized as a method for determining vacancy migration energies, first through electrical resistivity measurements [7, 8] and later, as has

been amply demonstrated by the work of Schaefer and co-workers [9], through PAS measurements.

The PAS technique emerged as the most effective technique in point defect studies because of its high resolution and nondestructive nature. PAS takes advantage of the fact that positively charged positrons tend to localize in open volume regions (e.g., free volume, vacancies, dislocations, voids, etc.), where there are missing positively charged atomic nuclei [10]. Furthermore when a positron and an electron annihilate the resulting gamma rays yield information about the annihilation site, making PAS a sensitive probe for vacancies. A positron-electron annihilation produces primarily two 511 keV gamma rays traveling in opposite directions.

Coincidence Doppler Broadening (CDB), a specific PAS technique, was used to characterize the defects in the specimens produced in this study. In CDB, the energies of the two 511 keV photons produced by the annihilation of a positron with an electron are measured simultaneously. Due to the momentum of the positron-electron pair prior to annihilation, the 511 keV photons may be blue-shifted or red-shifted [11]. The energy shift is given by:

$$\Delta E = \frac{1}{2} p_L c \qquad (1)$$

where p_L is the longitudinal component of the electron-positron momentum and c is the speed of light.

Two parameters are extracted from the CDB data; low momentum fraction, the normalized area under the central portion of the distribution (referred to as S in the positron literature), and high momentum fraction, the normalized area in a fixed interval under the high momentum tail of the distribution (referred to as W in the positron literature). The low momentum fraction parameter is due to positron annihilations with valence electrons, more likely to occur in regions with more open volume. The high momentum fraction parameter is due to positron annihilations with core electrons, more likely to occur when the positron is delocalized and not trapped in an open volume region. Thus the relative magnitudes of the low and high momentum fractions are good indicators of the defect concentration in a material, i.e. given the same bulk material, the sample with a higher low-momentum fraction and lower low momentum fraction has a higher defect concentration.

2. Experimental Procedure

Ni_3Ti ingots where obtained from ACI Alloys (San Jose, CA). The samples had a purity of 99.99%. The 100 mm long rods were sectioned perpendicularly to produce discs (6 mm diameter and 1 mm thick). The discs are polished using 1200 grit SiC metallographic paper and cleaned ultrasonically in acetone, to ensure good electrical and thermal contact with electrodes.

The ingots were then annealed in a system that allows the samples to be subjected to different DC current densities (ranging from 0 to 2546 $A.cm^{-2}$) at a constant temperature under a high vacuum (10^{-7} torr). The system contains a large (16.5 cm diameter and 6.5 cm long) cylindrical W mesh furnace surrounding the DC electrodes. The temperature range in this study was from 600-700°C, and the annealing time varied from 15 to 3000 min. Concerns regarding the validity of temperature measurements and other details of the experimental method are discussed in a previous publication [1]. After annealing, the samples were quenched by being dropped quickly from the furnace heat zone onto a water-cooled stainless steel plate.

CDB experiments were preformed using a setup similar to the one described in previous works [10, 11]. With this set-up, a 1 T magnetic field focuses positrons from a ^{22}Na source into a ~ 3 mm diameter spot. Positrons emitted from ^{22}Na sources have energies up to 546 keV, giving a typical implantation depth of the positrons into materials of up to 30 to 100 μm.

Low momentum fraction and high momentum fraction are not absolute parameters; they depend on the position and resolution of the photon detectors. However, the changes in these parameters are indicative of changes in defect concentrations.

3. Results

Figure 1 shows the change of the low momentum fraction with annealing time for samples annealed at 600°C without current, and a similar change for samples annealed with an applied current density of 1019 $A.cm^{-2}$. The zero-time data point is an average for the as-received (un-annealed) material (0.425 ± 0.0025), and the time scale, with a break, extends to 50 h. The as-received samples have a high low momentum fraction, indicative of high defect concentration, as is expected in a material which was synthesized by arc-melting and

subsequently quenched from a melt on water-cooled copper block. The data are compared in the figure to the fit of the equation:

$$S = A\exp\left(\frac{-t}{\tau_D}\right) + S_e \qquad (2)$$

where S is the low momentum fraction, t is time, τ_D is the rate of decay constant, A is a pre-exponential constant and S_e is approximately equal to the low momentum fraction the system is decaying to (i.e., equilibrium low momentum fraction). Figure 2 shows the normalized low momentum fraction data for 600 and 700^{o}C experiments with and without an applied current of 1019 A.cm^{-2}. In this case $\Delta S = S - S_e$ and $\Delta S_o = S_e - S_o$ where S_o is the low momentum value of the as-received sample. The fit to the data indicates that the low momentum fraction is decreasing exponentially with time with the decay constant, τ_D, providing a measure of the rate at which the defects are annealed out under the different conditions. The calculated values of this rate constant are 250.8, 52.5 , 26.4 , and 10.1 min for 600^{o}C- 0 A.cm^{-2}, 600^{o}C- 1019 A.cm^{-2}, 700^{o}C- 0 A.cm^{-2}, and 700^{o}C- 1019 A.cm^{-2}, respectively.

Electrical resistivity measurements where performed on the samples to corroborate the CDB results. These measurements show similar trends to the low momentum fraction vs, time data (**Figures 1 and 2**), with the resistivity decreasing exponentially with time.

Figure 3 is a plot of low momentum fraction vs. current density for samples annealed at 700^{o}C for 1 h. As in experiments in which the temperature was held constant but the time was varied (**Figures 1 and 2**), the low momentum fraction decreases with increasing current density. The samples become less defected with increasing current density as indicated by the decrease in the low momentum fraction.

4. Discussion

The rates of decay constants decrease significantly by the application of a current. At 600^{o}C it decreases from 250.8 min to 52.5 min and at 700^{o}C from 26.4 min to 10.1 min. The decrease represents a reduction by a factor of 4.7 and 2.6, respectively. **Figure 3** shows that increasing current density decreases the low momentum fractions for samples reacted at the same temperature for the same time.

The low momentum fraction, S, is directly related to the defect concentration provided that there is a singe type of defect (i.e. only mono vacancies, divacancies, etc.) where positrons are trapped and subsequently annihilated. **Figure 4** is a plot of the high

momentum versus the low momentum fractions for all the samples in this study. The linearity of the data suggests that there is a single type of defect with varying concentrations in the samples observed by positrons [10, 12]. In this case the low momentum fraction is directly proportional to the defect concentration in the sample so that it can be used much like electrical resistivity [7, 13] to analyze defect migration kinetics. While the nature of the defects cannot be ascertained from these results, we believe that the defects are single vacancies.

In metallic systems the rate of disappearance of non-equilibrium point defects (relaxation) at annealing temperature T, for annealing time t, is expected to given by:

$$\frac{dC}{dt} = C_1 \exp\left(\frac{-E_m}{k_B T}\right) \qquad (3)$$

where C is the point defect concentration, E_m is the migration energy of the defect, k_B is Boltzmann's constant, and C_1 is a constant. Because the low momentum fraction is directly proportional to the defect concentration, their rates of change are also proportional, so that at constant low momentum fractions, dS/dt values (from data in **Figure 2**) can be used to calculate the migration energy, E_m of the vacancies with and without an applied current. The calculated values are $E_m = 1.79 \pm 0.2$ eV without a current and $E_m^C = 1.36 \pm 0.1$ eV with an applied current; the vacancy migration energy decreased by 24% when a current was applied during annealing. The calculated vacancy migration energy values are consistent with reported vacancy migration energies in other intermetallics such as $Fe_{61}Al_{39}$, $Fe_{63}Al_{47}$ and Fe_3Al, with reported values of 1.7 ± 0.2, 1.7 ± 0.2, and 1.3 ± 0.1eV, respectively [9].

The influence of the current on defect mobility shown in this work is attributed to the electron wind effect [14-16]. In investigations on metallic systems, this effect is manifested by a directional dependence on the DC current. Experiments showing asymmetry in the growth of product layers with respect to the current direction have been observed in some cases but not in others, including the work referenced above [1]. The lack of asymmetry, in some cases, is a consequence of the complex nature of the diffusion process in ordered metallic compounds. For Ni_3Ti the diffusion of either element is coupled with that of the other so as to maintain structure and stoichiometry. This is supported by the relatively high activation energy for mobility calculated for the case in the absence of a current, 1.79 eV. Similar conclusions of a complex jump mechanism were arrived at for the $Fe_{60}Al_{40}$ system [9] on the basis of annealing experiments [17]. Complex jump mechanisms for ordered

intermetallic compounds have been proposed, including a six-jump cycle (Huntington-McCombie-Elock (HME) mechanism) [18-20], the antistructure bridge mechanism [21], and the α sublattice mechanism [22].

5. Summary and Conclusions

Samples of Ni_3Ti intermetallic were isothermally annealed at 600 and 700°C with and without an imposed DC current. The current increased the rate of the annealing out of point defects, as determined by coincidence Doppler broadening positron annihilation spectroscopy. The rate of increase was dependant on temperature and on the magnitude of the current density. Calculations of the mobility activation energy demonstrated a significant reduction in this value as a result of the application of a current, a 24% reduction from 1.79 ± 0.2 to 1.36 ± 0.1 eV. The work represents the first direct evidence of the role of the current in the mobility of point defects in intermetallic systems.

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Figure Captions:

Figure 1: Low momentum fraction, S, as a function of time for samples annealed at 600^{o}C with and without a DC current of 1019 A.cm^{-2}.

Figure 2: Normalized change in low momentum fraction $\Delta S/\Delta S_o$ as a function of time for samples annealed at 600 and 700°C under current densities of 0 and 1019 A.cm^{-2}.

Figure 3: Low momentum fraction vs. current density for sample annealed at 700°C for 60 min.

Figure 4: Low momentum fraction vs. high momentum fraction for all samples.

Figures:

Figure 1

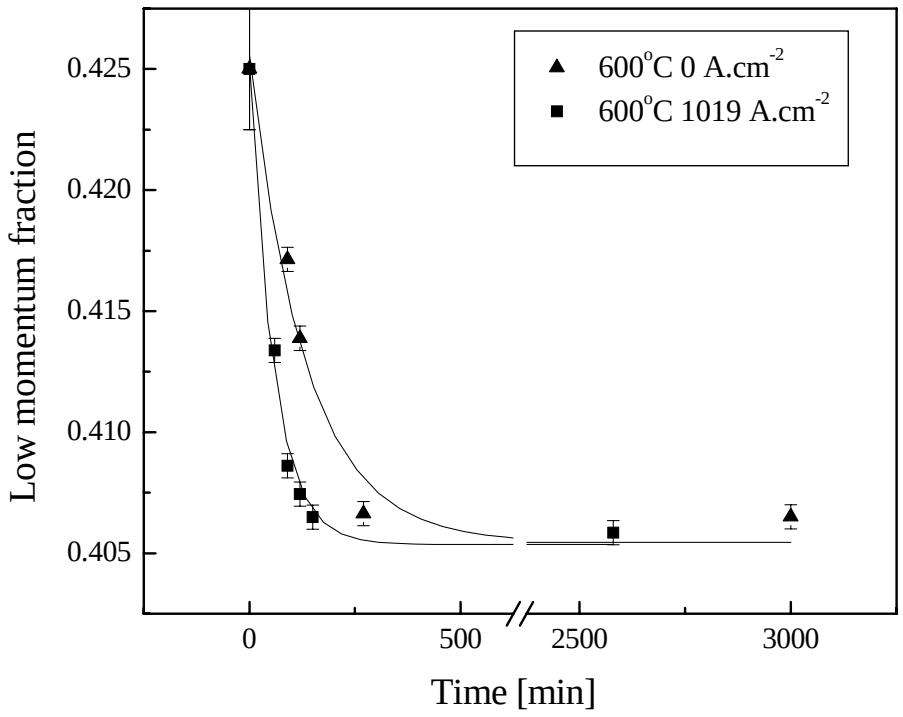


Figure 2

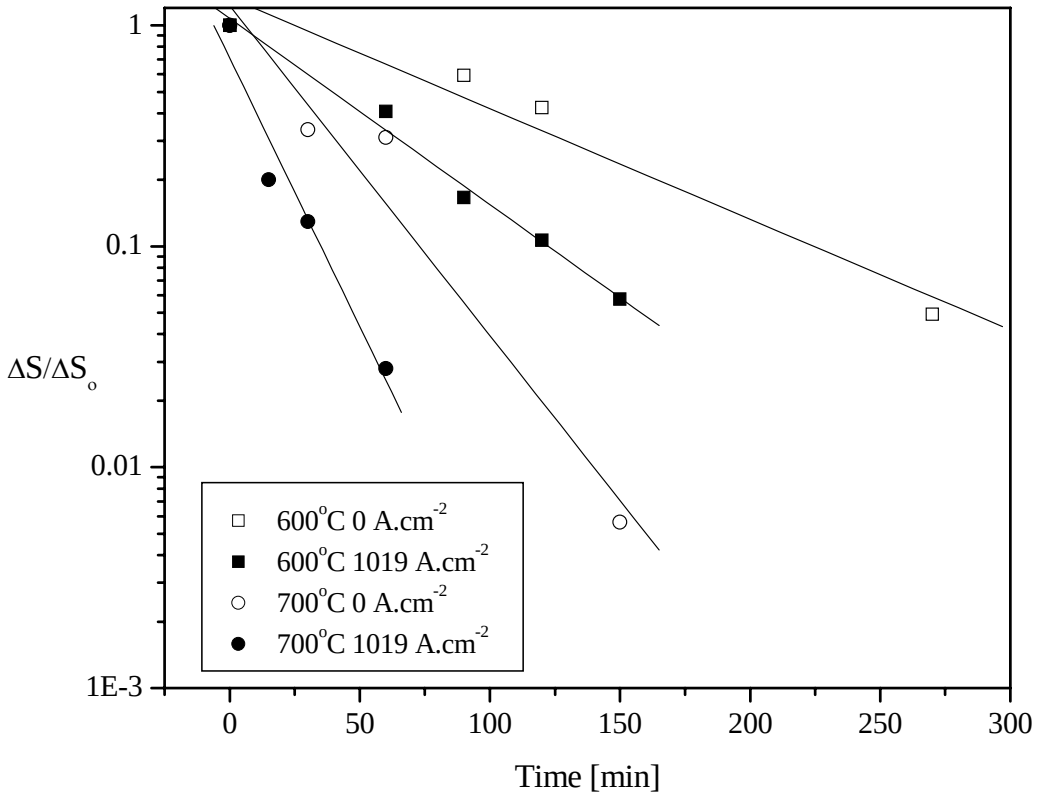

1
0.1
0.01
1E-3
ΔS/ΔS$_o$
0
50
100
150
200
250
300
Time [min]
600°C 0 A.cm^{-2}
600°C 1019 A.cm^{-2}
700°C 0 A.cm^{-2}
700°C 1019 A.cm^{-2}

Figure 3

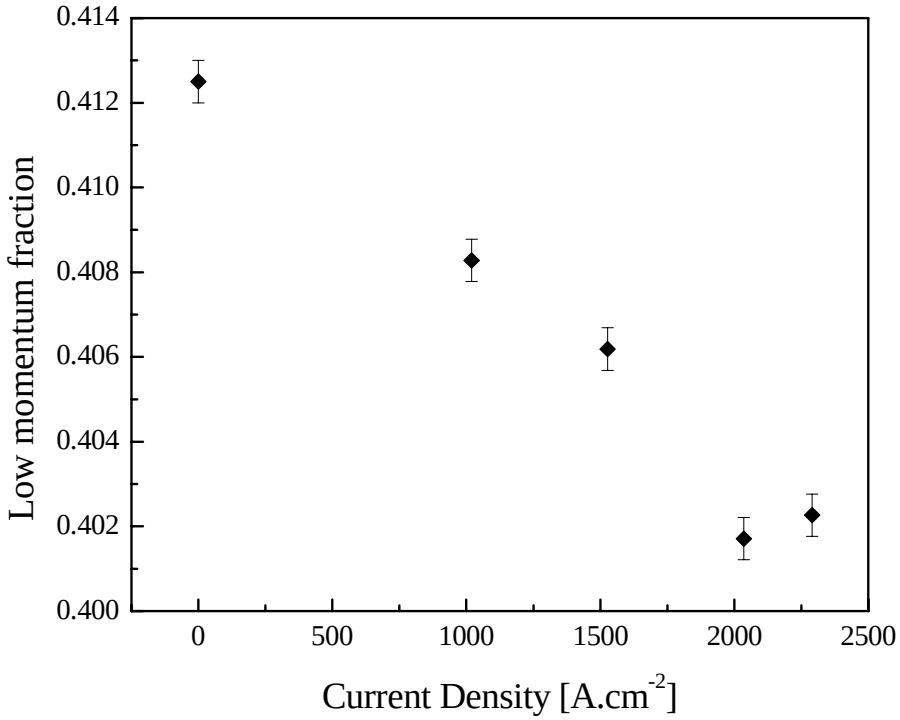
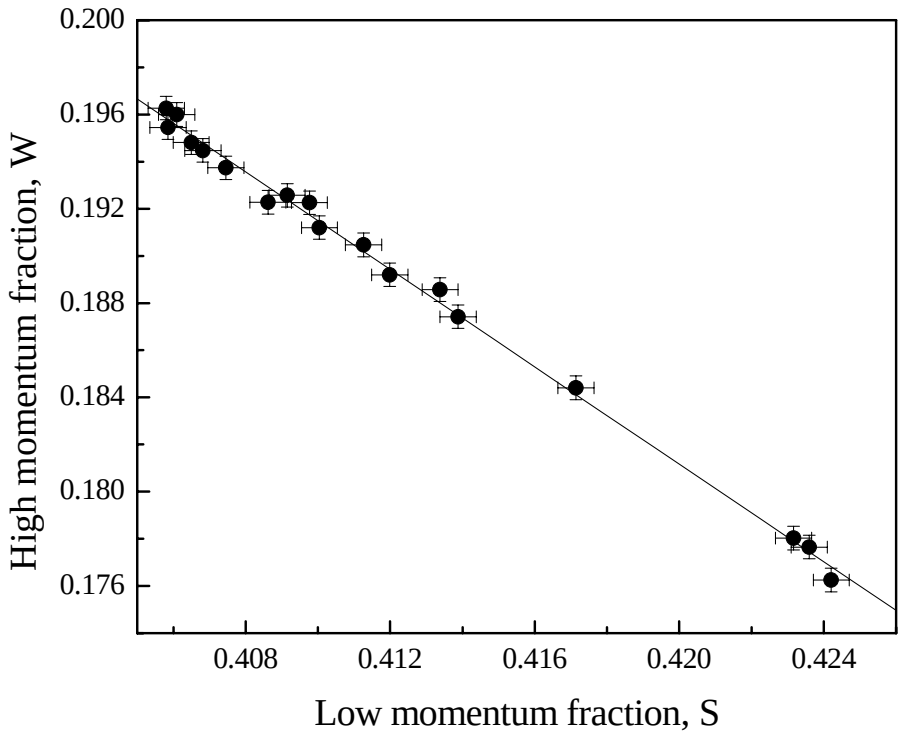

0.414
0.412
0.410
0.408
0.406
0.404
0.402
0.400
Low momentum fraction
0
500
1000
1500
2000
2500
Current Density [A.cm-2]

Figure 4


0.200
0.196
0.192
0.188
0.184
0.180
0.176
High momentum fraction, W
0.408
0.412
0.416
0.420
0.424
Low momentum fraction, S